A mathematical model of emulsion polymerization

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1. Introduction

We consider a mathematical model of polymerization which in the language of chemistry is called emulsion polymerization. Roughly speaking, polymerization is the formation of huge molecules (–the molecules of the polymer–) from smaller ones (–the molecules of the monomer). In the case of emulsion polymerization this process takes place in an aqueous medium in the presence of appropriate auxiliary substances. As an example we mention that the well–known polymer polyvinyl chloride (PVC) can be produced in this way starting from the monomer vinyl chloride.
There are different possibilities to operate a polymerization reactor. One distinguishes batch (or discontinuous) and continuous reactors. The batch reactor is one where all ingredients are charged at the beginning of the polymerization and the reaction proceeds over a certain interval of time. Continuous reactors run with a continuous inflow and outflow of material. Mixed types of reactor operating are possible, e.g. the semibatch mode where part of the ingredients are added during the polymerization process. A general assumption is that the content of the reaction vessel is well stirred so that local inhomogeneities can be neglected.
The mathematical model presented here was proposed in the seventies by Min and Ray ([12], [13], [14]). It has been modified and extended in the research group of Dr. Tauer ([20], [21] , [22]) at the (former) Institute of Polymer Chemistry (Teltow–Seehof). At the (former) Karl Weierstrass Institute of Mathematics (Berlin) the model has been investigated from the mathematical and numerical point of view during several years ([4], [5], [6], [7]).

2. The mathematical model

To describe the polymerization process we introduce a particle size distribution function $f = f(t,v)$ depending on time $t \geq 0$ and a volume variable $v \geq 0$. The physical interpretation of f may be given in a heuristic way as follows: The differential $f(t,v)dv$

is the average number of particles (or proportional to the average number of particles) whose volumes at time t belong to the infinitesimal volume interval $(v, v+dv)$. That is, we make the usual assumption of statistical physics that the particle number has a density – which is justified by the large number of particles.

The time evolution of f is is influenced by chemical and physical processes like particle growth, particle coalescence, particle nucleation, the effect of additional substances (e.g. catalyzers and emulsifiers) and the reaction conditions. For the more chemical and physical side of the quite complicated interplay of all these factors we refer to the papers mentioned in the introduction.

Important quantities to characterize the particle size distribution function f are the moments M_α of order α, defined by

$$M_\alpha(f)(t) = \int_0^\infty v^\alpha f(t,v)dv.$$

Especially, we interpret

$$\begin{aligned} M_0(f)(t) &= \int_0^\infty f(t,v)\,dv && \text{as particle number ,} \\ M_1(f)(t) &= \int_0^\infty v f(t,v)\,dv && \text{as mean particle volume ,} \\ M_{2/3}(f)(t) &= \int_0^\infty v^{2/3} f(t,v)\,dv && \text{as mean particle surface .} \end{aligned}$$

For the comparison with experiments the essential quantity is

$$Q(t,v) = \frac{\int_0^v w f(t,w)\,dw}{\int_0^\infty w f(t,w)\,dw},$$

i.e. the relative contribution of particles of volume $\le v$ to the mean particle volume at time t.

The model equation is formally a first order partial differential equation for f of the form

$$\frac{\partial f}{\partial t} + \frac{\partial (rf)}{\partial v} + a(f-g) = K(f)\,, \tag{2.1}$$

which we consider on $t>0$, $v>0$ with the initial condition

$$f(0,v) = f_0(v), \quad v \ge 0, \tag{2.2}$$

and the boundary condition

$$f(t,0) = 0, \quad t \ge 0. \tag{2.3}$$

The initial value f_0 is a given nonnegative function satisfying the compatibility condition $f_0(0)=0$; the boundary condition (2.3) simply says that there are no particles of volume zero. By physical reasons one has to claim $f(t,v) \ge 0$ for $v \ge 0$, $t \ge 0$; and the asymptotic behaviour $f(t,v) \to 0$ for $v \to \infty$.

The main constituents in the model equation are

$r = r(v, f)$	the particle growth rate,
$K(f)$	the coalescence term,
$g = g(v)$	the given seed particle number distribution function.

The constant a is proportional to the reciprocal of the mean residence time.

The particle growth rate $r = r(v, f)$ is an expression of the form

$$r(v, f) = r_0(M_0(f), M_1(f))(b_1 v + b_2 v^{4/3})^{1/2} \tag{2.4}$$

where b_1, b_2 are given nonnegative constants and r_0 is a given nonnegative function. This is an empirical formula describing particle growth by chemical reactions between monomer and polymer particles.

The coalescence term is defined by

$$K(f)(v) = \frac{1}{2}\int_0^v k(v-w, w) f(v-w) f(w) dw \; - \; f(v) \int_0^\infty k(v, w) f(w) dw \tag{2.5}$$

with a given coalescence kernel k . Following the proposals in [12], [13], [14], [20], [21] we take

$$k = k(v, w) = C(v\,w)^{-1/3}, \quad v, w \; > \; 0, \tag{2.6}$$

i.e., a symmetric, positive and weakly singular (integrable) kernel with a given coalescence constant C .

All these terms show that the model (in its simplest form) is a nonlocal first– order partial integro–differential equation.

3. Discussion of the model

To see that the model works properly it is instructive to consider several special cases. Putting the constant $a = 0$ we have the case of a batch reactor described by

$$\frac{\partial f}{\partial t} + \frac{\partial (r f)}{\partial v} = K(f) \; . \tag{3.1}$$

A simple calculation shows that the coalescence term $K(f)$ satisfies

$$\begin{aligned} \int_0^\infty K(f)(v) dv &= -\frac{1}{2}[M_{-1/3}(f)]^2 \; , \\ \int_0^\infty v K(f)(v) dv &= 0 \; . \end{aligned}$$

Using this and assuming f nonnegative, we obtain from (3.1) by a simple calculation, taking into account the boundary condition (2.3) and the asymptotics as $v \to \infty$:

$$\dot{M}_0(t) = \frac{d}{dt} M_0(t) \leq 0, \quad \dot{M}_1(t) = \frac{d}{dt} M_1(t) \geq 0.$$

This is just the expected behaviour – the particle number decreases, the average particle volume increases with growing time. Reducing the model further by omitting the coalescence term we obtain with the simplified growth rate

$$r = r_0(M_0(f), M_1(f))$$

the model equation

$$\frac{\partial f}{\partial t} + r_0(M_0(f), M_1(f))\frac{\partial f}{\partial v} = 0. \tag{3.2}$$

In this case the particle number is conserved, i.e., with appropriate scaling we have

$$M_0(f)(t) = M_0(f_0) = 1.$$

With the initial condition $f(0, v) = f_0(v)$, continued formally by $f_0(v) = 0$ for $v < 0$, we can solve (3.2) by the method of characteristics. We get

$$f(t, v) = f_0(v - (M_1(t) - 1)),$$

where M_1 is the solution of the initial value problem

$$\dot{M}_1 = r_0(1, M_1), \quad M_1(0) = 1.$$

Another reduced version of the model equation we obtain by putting $r = 0$, i.e. the case of pure coalescence. Then (3.1) becomes

$$\frac{\partial f}{\partial t} = K(f), \quad f(0, v) = f_0(v). \tag{3.3}$$

This is the well–known integro–differential equation of coagulation which describes a lot of processes where particles are lumped together (beyond colloid chemistry e.g. in biology, meteorology). Formal integration gives

$$\dot{M}_0(t) \leq 0, \quad \dot{M}_1(t) = 0,$$

i.e. the number of particles decreases and the mean particle volume M_1 is conserved. Equation (3.3) has been considered e.g. in [1], [2], [8], [9], [10], [11], [15], [17], [18], [19].This equation allows to clarify the rôle of the coalescence term

$$K(f)(v) = \frac{1}{2}\int_0^v k(v - w, w)f(v - w)f(w)dw \; - \; f(v)\int_0^\infty k(v, w)f(w)dw.$$

Speaking heuristically, the left hand side of (3.3) is the time rate of change of the number of particles of volume v . The right hand side says that particles of volume v are formed from particles of volume $w < v$ and of volume $v - w$ in a symmetric manner (which explains the factor $1/2$), and they disappear if particles of volume v agglomerate with particles of volume $w > 0$, where the intensity of agglomeration is characterized by the coalescence kernel $k = k(v, w)$. This interpretation of the balance equation (3.3) for pure coalescence goes back to Smoluchowski (see e.g. [16]).

4. Model extensions

For the actual calculations the simplified model described above has to be extended. We discuss two variants, without going too deep into the quite involved chemical details. The main additional ingredient is the so called nucleation term which takes into account the more physical process of nucleation. By nucleation appear particles of a definite size by transformation of water soluble oligomers into particles.

Variant 1. The model equation has the form

$$\frac{\partial f}{\partial t} + \frac{\partial (r(f) f)}{\partial v} + a(f - g) = K(f) + N(f; v) \tag{4.1}$$

where $N(f; v)$ is denotes the nucleation term. This term depends on the

initiator concentration I ,
emulsifier concentration E ,
water volume fraction V ,

which are functions of the time. The nucleation term has the form

$$N(f; v) = c_1 (1 - I(t))\, V(t)\, (1 + \frac{E(t)}{c_2})\, \delta(v - v_0)$$

where $\delta(v - v_0)$ denotes Dirac's Delta–distribution with support v_0 .
The initiator is a substance which furnishes the radicals necessary to initiate the polymerization reaction, the emulsifier is a substance necessary to stabilize the growing polymer particles. The initiator concentration is assumed to satisfy the simple differential equation

$$\frac{dI}{dt} = c_3 - c_4\, I, \quad I(0) = I_1,$$

which gives

$$I(t) = c_3/c_4 + (I_1 - c_3/c_4)\, e^{-c_4\, t}.$$

The total emulsifier concentration $S = S(t)$ is given by

$$S(t) = S_0 (1 - e^{-at})$$

and splits into the free emulsifier concentration in water $E = E(t)$ and emulsifier covering the polymer particles. Introducing the quantity $A = A(t)$ – the degree of coverage of particle surface with emulsifier –, we have the balance equation

$$E(t) + p_0\, A(t)\, M_{2/3}(f) = S(t).$$

Here appears the moment of order $2/3$ which can be interpreted as mean particle surface (see Section 2). The free emulsifier in water and the emulsifier on the particle surface are linked by an adsorption isotherme

$$A = \frac{p_1\, E}{1 + p_2\, E}$$

of Langmuire type.
The water volume fraction $V = V(t)$ satisfies the balance equation

$$V(t) + H_0(t)[1 - x(1-q)] = 1, \quad \text{where} \quad H_0(t) = B(1 - \exp(-t/T)).$$

Here denotes $x = x(t) = R(M_1(f))$ the conversion, where R is the rational function

$$R(z) = \frac{a_0 z}{b_0 z + c_0},$$

and $q = d_m/d_p$ is the ratio of monomer and polymer density. The constant B and the mean residence time T are given constants as well as the quantities p_0 , p_1 , p_2 , S_0 , a_0 , b_0 , c_0 , c_1 , c_2 , c_3 , c_4 used above.
The part r_0 in the factorized form of the particle growth rate (see (2.4)) has the form

$$r_0(M_0(f), M_1(f)) = \frac{A_0(M_1(f))}{\sqrt{M_0(f)}} \tag{4.2}$$

where

$$A_0(M_1(f)) = \begin{cases} A_1 & \text{if} \quad x = R(M_1(f)) \le R_0 \\ A_2(x) & \text{if} \quad x = R(M_1(f)) > R_0 \end{cases}$$

with

$$A_2(x) = c_5 \, \frac{1-x}{qx}.$$

The constant c_5 is given and we have the continuity condition

$$A_1 = A_2(R_0).$$

Variant 2. Compared with variant 1 we modify the nucleation term and the particle growth rate. Both become conversion dependent and also the coalescence constant is substituted by a conversion dependent quantity. This modification allows to take into account the gel effect and the glass effect. These effects appear as the polymerization progresses and are a consequence of the growing viscosity of the reactor content. If the conversion is sufficiently high, both particle growth rate and coalescence term disappear. The nucleation term gets the form

$$N(f; v) = c_1 P(t) \, V(t) \, (1 + \frac{E(t)}{c_2}) \, \delta(v - v_0),$$

where $P = P(t)$ denotes the concentration of water soluble oligomers which satisfies the initial value problem

$$\frac{dP}{dt} = c_6 \, I - \{ \, c_7 \, [\, 1 - A(t) \,] \, M_{2/3}(f) \left(\frac{M_0(f)}{M_1(f)} \right)^{1/3} + \, c_8 \, \} \, P, \quad P(0) = 0. \tag{4.3}$$

The term r_0 in (4.2) is substituted by

$$r_0(M_0(f), M_1(f)) = C_0(x)\,\frac{A_0(M_1(f))}{\sqrt{M_0(f)}},$$

where

$$C_0(x) = \begin{cases} 1 & \text{if} \quad x \le R_0\,, \\ c_9\,\dfrac{1-x(1-q)}{1-x} & \text{if} \quad R_0 < x < R_1\,, \\ 1-x & \text{if} \quad R_1 \le x < R_2\,, \\ 0 & \text{if} \quad R_2 \le x\,. \end{cases}$$

The coalescence constant C which appears in the coalescence kernel (see (2.6)) is substituted by a conversion dependent function $C = C(x)$ of the following form:

$$C(x) = \begin{cases} 1 & \text{if} \quad x \le R_0\,, \\ c_9\,\dfrac{1-x}{1-x\,(1-q)} & \text{if} \quad R_0 < x < Q_1\,, \\ 0 & \text{if} \quad Q_1 \le x\,. \end{cases}$$

Again are $c_5\,, c_6\,, c_7\,, c_8\,, c_9\; R_0\,, R_2\,, Q_1$ given constants.

5. Numerics

We sketch only the main ideas. For the approximate solution of the model equation (4.1) we use a difference method. Instead of the volume variable v we take the diameter D as one of the independent variables, linked with v by $v = (\pi/6)D^3$. We discretize the time variable t and the diameter variable D by the (not necessarily equidistant) grid (t_i, D_k) where

$$0 = t_0 < t_1 < ... < t_i < ... < t_M, \quad 0 = D_0 < D_1 < ... < D_k < ...D_N$$

and denote the corresponding step size by $\tau_i = t_{i+1} - t_i$ and $h_k = D_{k+1} - D_k$, respectively. We put f_k^i for the value of a function defined on the grid in the grid point (t_i, D_k) and take

$$f_k^i \;\approx\; f(t_i, D_k)$$

as an approximation of (e.g.) the particle density in (t_i, D_k) . We split the coalescence term (2.5) (omitting the time variable)

$$K(f)(v) = H(f)(v) - f(v)G(f)(v), \quad \text{where} \quad G(f)(v) = f(v)\int_0^\infty k(v,w)f(w)dw.$$

To formulate a difference method, we follow the philosophy of "as implicit as possible, as explicit as necessary". Denoting by

$$R_k^i \approx r(f(t_i, D_k)) \ , \ N_k^i \approx N(t_i, D_k) \ , \ H_k^i \approx H(f)(t_i, D_k)) \ , \ G_k^i \approx G(f)(t_i, D_k)$$

approximations of the particle growth rate, the nucleation term and the splits of the coalescence term, we discretize the model equation by

$$\frac{f_k^{i+1} - f_k^i}{\tau_i} + \frac{1}{h_{k-1}} \left(R_k^i \ f_k^{i+1} - R_{k-1}^i \ f_{k-1}^{i+1}\right) + a \left(f_k^{i+1} - g_k\right) = N_k^i + H_k^i - f_k^{i+1} G_k^i \qquad (5.1)$$

for $k = 1, 2, ..., N$; the boundary condition (2.3) gives $f_0^{i+1} = f_0^i = 0$. The computational scheme runs as follows: Assume that all quantities are calculated in the grid points D_k ; $k = 0, 1, ..., N$ on the time level t_i . From the difference approximation (5.1) and the boundary condition we find (first) approximations for f_k^{i+1} on the new time level t_{i+1} in a knitting–like manner for $k = 0, 1, .., N$. Then we compute by numerical integration the nonlocal quantities like moments and the components of the coalescence term. An implicit difference scheme (Euler backward) is used to find an approximate solution of (4.3) on the time level t_{i+1} :

$$\frac{P^{i+1} - P^i}{\tau_i} = c_6 \, I(t_{i+1}) - \Phi(t_{i+1}) \, P^{i+1}, \quad P^0 = 0, \qquad (5.2)$$

where Φ is an approximation

$$\Phi(t_{i+1}) \approx c_7 \left[1 - A(t_{i+1}) \right] M_{2/3}(f)(t_{i+1}) \left(\frac{M_0(f)(t_{i+1})}{M_1(f)(t_{i+1})} \right)^{1/3} + \ c_8$$

calculated from the values available at this stage of the calculation. Using the P^{i+1} in (5.1) we find a second approximation for the f_k^{i+1} . This procedure is iterated until the differences between corresponding quantities are sufficiently small. That is, we solve (5.1), (5.2) by a quite simple iteration method. If certain convergence criteria are satisfied, we update and go on to the next time level t_{i+2} . The stopping criteria for the iteration process as well as the step size for the time and the diameter variable were found by numerical experiments, supported by heuristics from polymer chemistry.

REMARK 1. The most complex term is the convolution part H of the coalescence term:

$$H(f)(v) = \frac{1}{2} \int_0^v k(v - w, w) f(v - w) f(w) \, dw.$$

Transformed to the diameter scale its value at the grid point D_k, $k \geq 1$, is

$$(H(f))_k = 3(\pi/6)^{1/3} \int_0^{\Theta_k} (D_k^3 - y^3)^{-1/3} \, y f(\frac{\pi}{6}(D_k^3 - y^3)) \, f(\frac{\pi}{6} y^3) \, dy,$$

where $\Theta_k = 2^{-1/3} D_k$ and simple symmetry properties of the convolution are used. This expression is approximated using a quadrature formula of trapezoidal type – we omit the

details.
Another possibility to calculate H assumes an equidistant grid in the volume variable v, given by $v_k = k\Delta v$, $k = 0, 1, ...N$. Then a natural approximation of H is given by

$$(H(f))_k \approx \frac{\Delta v}{2} \sum_{j=0}^{k} F_{k-j} F_j, \quad k = 1, 2, ...; \ (H(f))_0 = 0$$

where $F_0 = 0$, $F_k = v_k^{-1/3} f_k$ for $k > 1$. The convolution sum on the right hand side can be calculated using the fast Fourier transform (FFT). Unfortunately, the necessary switching from a non–equidistant D –grid to an equidistant v –grid spoils somewhat the advantages of FFT.

6. Asymptotics

In the following considerations we deal exclusively with Variant 1. In the case of a continuous reactor one expects that the time evolution leads to an asymptotic state as $t \longrightarrow \infty$, i.e. all quantities involved in the process assume their corresponding asymptotic values. Especially we have $S(t) \longrightarrow S_0, H(t) \longrightarrow B, I(t) \longrightarrow c_3/c_4$ as $t \longrightarrow \infty$. Denote by E_∞, V_∞ the asymptotic values of $E(t), V(t)$ and by $M_{0,\infty}, M_{1,\infty}, M_{2/3,\infty}$ the asymptotic values of the corresponding moments. In addition we assume that

$$b_1 = 0, \quad g(v) = 0,$$

i.e. the particle growth rate has a special structure and there is no seed. (This is the situation met in all examples.) Multiplying the model equation (4.1) by v and integrating over $(0, \infty)$ we get

$$aM_{1,\infty} - \frac{A_0(M_{1,\infty})}{\sqrt{M_{0,\infty}}} \sqrt{b_2}\, M_{2/3,\infty} = Cv_0, \quad C = c_1 \left(1 - \frac{c_3}{c_4}\right) V_\infty \left(1 + \frac{E_\infty}{c_2}\right).$$

Here is C the (asymptotic) factor in the nucleation term and v_0 the support of the Dirac distribution.
If we in addition assume that there is no coalescence, the asymptotic model equation corresponding to (4.1) becomes

$$P \frac{\partial(v^{2/3} f)}{\partial v} + af = C\delta(v - v_0), \quad P = \frac{A_0(M_{1,\infty})}{\sqrt{M_{0,\infty}}} \sqrt{b_2}. \tag{6.1}$$

This equation has the solution

$$f(v) = \frac{C}{P} v^{-2/3} \exp\left(\frac{3a}{P}(v_0^{1/3} - v^{1/3})\right) H(v - v_0), \tag{6.2}$$

where H denotes Heaviside's function

$$H(y) = \begin{cases} 0 & \text{if } y < 0, \\ 1 & \text{if } y > 0. \end{cases}$$

These relations are useful tools to control the computation.

7. Regularization of singular initial states

It is quite natural to start from the "reactor filled with initiator water", which corresponds in the mathematical model to the assumption of a vanishing initial distribution:

$$f_0(v) = 0.$$

In this case we have a singularity in the growth term (4.2) resulting from $M_0(f_0) = 0$. To overcome this difficulty we try an expansion of the form

$$f(t,v) = t^\alpha b_0(v) + o(t^\alpha).$$

with an appropriate positive power α . The coalescence term will be neglected because of $K(f) = O(t^{2\alpha})$, which is in good agreement with the fact that in the early stages of the polymerization coalescence is unimportant. We have in the nucleation term

$$V(0) = 1, \quad E(0) = 0, \quad 1 - I(t) = B\,t + \ldots .$$

We take $\alpha = 2$ and enter with all assumptions into (4.1). Comparison of equal powers of t (– details are omitted –) gives the following equation for the coefficient b_0 of the lowest order term:

$$2b_0(v) + \frac{A_1}{\sqrt{M_0(b_0)}} \frac{\partial(v^{2/3} f)}{\partial v} = c_1 B \delta(v - v_0), \quad \text{where} \quad 2M_0(b_0) = c_1 B.$$

This is formally the same equation as (6.1). So we can use the solution (6.2) to overcome the (mathematical) difficulties in the early stage of the polymerization.

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